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Title

[電気二重層コンデンサー用分極性電極の製造方法]

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Specification

1. Title of the invention

Manufacturing method of polarized electrode for double layer electrical capacitor

2. Scope of the patent claim

(1). polarized electrode for double layered electrical capacitor characterized such that first, the kneaded matter of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shapes, then, liquid lubricant is removed, next, preformed compact is formed by heated rolling roll into a specified thickness.

(2). The manufacturing method of polarized electrode for double layered electrical capacitor characterized such that the kneaded matter of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape, the amount of liquid lubricant in preformed compact is adjusted to be 10~47 wt%, next, preformed compact is formed into a specified thickness by rolling roll, after that, liquid lubricant is removed.

(3). the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that kneaded matter of fine powder of carbon, fluorine containing polymer resin, liquid lubricant is preformed into sheet shapes, then the liquid lubricant in preformed compact is adjusted to be 10~47 wt%, then, next, preformed compact is formed by heated rolling roll into a specified

thickness, after that, liquid lubricant is removed

(4). the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that first, the kneaded matter of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape, preformed compacts themselves are piled up using the ends, adhered by rolling, formed into a continuous long preformed compact, after that, liquid lubricant is removed, and preformed compact is formed by heated rolling roll into a specified thickness.

(5). the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that first, the kneaded mixture of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape, preformed compact themselves are piled up using the ends, adhered by rolling, formed into a continuous long preformed compact by rolling, after that, preformed compact is formed by heated rolling roll into a specified thickness,

Amount of liquid lubricant in preformed compact is adjusted to be 10~47 wt%,

Next, preformed compact is formed into a specified thickness by rolling roll,

After that, liquid lubricant is removed.

(6). the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that first, kneaded

mixture of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape, preformed compact themselves are piled up using the ends, adhered by rolling, formed into a continuous long preformed compact,

Amount of liquid lubricant in the preformed compact is adjusted to be 10~47 wt%,

after that, preformed compact is formed by heated rolling roll into a specified thickness,

after that, liquid lubricant is removed.

(7).the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that first, kneaded mixture of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape, after that,

Amount of liquid lubricant in the preformed compact is adjusted to be 20~47 wt%,

Preformed compact themselves are piled up using the ends, adhered by rolling, formed into a continuous long preformed compact,

Next, preformed compact are formed into a specified thickness by rolling roll, after that,

Liquid lubricant is removed.

(8).the manufacturing method of polarized electrode for double layered electrical capacitor characterized such that first, kneaded mixture of fine powder of carbon, fluorine containing polymer resin and liquid lubricant are preformed into sheet shape,

Amount of liquid lubricant in the preformed compact is adjusted to be 20~48 wt%,

Preformed compact themselves are piled up using the ends, adhered by rolling, formed into a continuous long preformed compact, Next, preformed compact are formed into a specified thickness by heated rolling roll,

After that, liquid lubricant is removed.

3. Detailed invention of the invention

[Utilized fields in industry]

Present invention relates to the manufacturing method of polarized electrode for double layered electrical capacitor.

[Prior arts]

Referring to figure 4 and figure 5, the outline of double layered electrical capacitor is explained.

As shown in figure 5, regarding double layered electrical capacitor, when it is made into a product, in general, a plural number, e.g., 5 units of capacitor cells 2 are stacked up concentrically, and takes the form of being housed in a cup shaped case.

Each capacitor cell 2 are disk shaped, and as shown in figure 4, is equipped with a pair of polarized electrode 4a and 4b, a separator 5, ring shaped gasket 6, and a pair of current collector 7a and 7b which are thermally adhered to the top and bottom surface of gasket 6.

In explaining more in details, polarized electrode 4a and 4b includes solid carbon compact, and is mutually isolated by electrically insulated separator 5. Separator 5 is composed of finely porous film of polyolefin type, or unwoven cloth or paper, preferably, the riser part is formed on its peripheral part. This riser part surrounds one side of polarized electrode 4b, thereby, this prevents the polarized electrode 4a and 4b themselves from been short circuited at each peripheral part. And, polarized electrode 4a and 4b and separator 5 are mutually anchored by the adhesive agent 8 provided partially on the mutual interface. Polarized electrode 4a and 4b and separator 5 are impregnated with the electrolyte such as 50wt% sulfuric acid water solution.

Gasket 6 is formed by integrating into one the low density polyethylene layer 10a and 10b for instance, on both sides of ethylene. Propylene sulfuric acid rubber substrate 9. And, current collector 7a and 7b is composed of polyethylene film which provides conductivity by carbon materials such as for instance carbon black, and this not only functions as the electrical conductive means between polarized electrode 4a and 4b, but also functions to seal air tightly the polarized electrode 4a and 4b and separator 5 inside of the gasket 6.

Capacitor cell 2 structured as described above, as shown in figure 5, are stacked up using necessary quantity (e.g., 5 units) to meet the rated voltage, and is integrated into one by surrounding

its surroundings by air tightly insulated, thermal contraction tube 11. Cell assembly 12 thus integrated into one is housed inside case 3 in the pressurized condition.

Highly conductive resin or rubber elastic conductive plate 13a and 13b are positioned such that it contacts the upper and lower surface of cell assembly 12 inside the case 3. And, over the upper side elastic conductive plate 13 is positioned terminal assembly 14. Terminal assembly 14 is equipped with 2 pieces of terminal 15a and 15b consisting of metal plate and these are assembled via insulation plate 16. Terminal 15a is connected electrically on the upper surface of cell assembly 12 via elastic conductive plate 13a. And, terminal 15b contacts the upper end of case 3 hence, is electrically connected to the lower surface of cell assembly 12 via case 3 and elastic conductor plate 13b. As made clear from such electrical connection status, electric conductor plate 13a and 13b functions such that they respectively reduce the contact resistance between upper surface of cell assembly 12 and the terminal 15a, and the lower part of cell assembly 12 and the bottom surface of case 3, thus stabilizing the electrical connection.

And, in order to cover the opening part of case 3, opening sealing resin 17 is provided. Opening sealing resin 17 is used to air tightly seal the inside of case 3 air tight in order to provide washing proof vis-à-vis said double layered electrical capacitor. And, over the outer circumference surface of the case 3, in order to cover for

insulation, thermal contraction tube 18 is capped.

[Problem the invention attempts to solve]

When the miniaturization of above described double layered electrical capacitor, particularly, height reduction (the height dimension H in figure 5 is reduced) is attempted, each capacitor cell 2 which constitutes cell assembly 12 have to be made thinner. In order to attempt to make the capacitor 2 thinner, the most effective method is to make into thin film the polarized electrode 4a and 4b (turn into a sheet).

Traditionally, polarized electrode which uses sheet shape was produced using the method in which rubbery viscous blending product composed of fine carbon powder (active carbon/ or carbon black), polytetra fluoro ethylene (PTFE) resin and liquid lubricant is compacted into sheet shape by rolling roll. As liquid lubricant, water, alcohol, and glycol are used.

However, regarding above described method, when the attempt is made to make thickness of the sheet thinner, due to the adhesive strength of liquid lubricant and the stretching by the rubber elasticity of blending product, sheet pile ups and stick together, hence, its handling was impossible in substance. Because of this, the lower limit of sheet thickness that can be produced was set at 0.6mm.

As a means to solve above described problem, one can consider that, first, the sheet shaped preformed compact with a certain

thickness is obtained, and liquid lubricant is removed from this preformed compact, then, this is turned a thin film using the ends by rolling roll. However, even by this method, if one wants to obtain one with 0.6mm or less in thickness, in the final analysis, cracking were produced, or turned into pieces by rolling roll, hence making the production impossible.

Hence, a method was proposed (Patent disclosure showa 63-107011 gazette) wherein after removing the liquid lubricant from sheet shaped preformed compact, this compact is subject to stretching treatment in an axis direction or multiple axis.

According to this method, sheets with thickness 0.6mm or less can be produced. However, according to this method, after pressurized process, drawing process is added, hence, this makes the processes complicated, and it takes a long time for drawing process, because of these standpoint, this method is not suitable for industrialization.

Hence, the purpose of present invention is to provide the manufacturing method of polarized electrode for double layered electrical capacitor in which making thin film of polarized electrode related to the height reduction of double layered electrical capacitor is enabled with higher productivity.

[Means to solve the problem]

In order to solve the above described technical problems, there are several phases as described below. In each phase, according to the

manufacturing method of the polarized electrode relating to present invention, first of all, a step (starting step) is executed in which the kneaded product of fine carbon powder, fluorine containing polymer resin and liquid lubricant is preformed into sheet shape.

Regarding the first situation (claim item 1) of present invention, after the aforementioned start step, the following each steps are provided;

- 1-a. Liquid lubricant is removed,
- 1-b. Next, preformed compact is formed into a specified thickness by heated rolling roll.

According to the second phase (claim item 2) of present invention, after the aforementioned starting step, each of the following steps is provided;

2-a. amount of liquid lubricant in preformed compact is adjusted to be 10~47 wt%,

2-b. Next, preformed compact is formed into a specified thickness by rolling roller,

2-c. after that, liquid lubricant is removed.

At the third phase of present invention (claim item 3), replacing step (2-b) at above described phase 2, the following step is executed.

3-b. Next, preformed compact is formed into the specified thickness by heated rolling roll.

As the fourth phase (claim item 4) of present invention, after the aforementioned starting step, each of the following steps is

executed;

4-a. Preformed compact themselves are piled up using the ends, adhered by pressurization and made into continuous long preformed compact, then,

4-b. liquid lubricant is removed,

4-c. Next, preformed compact is formed into a specified thickness by heated rolling roll.

At the fifth phase (claim item 5) of present invention, replacing the above described fourth phase, step [4-b]~[4-c],

Each of the following is executed;

5-b. Amount of liquid lubricant in preformed compact is adjusted to be 10~47 wt%,

5-c. next, preformed compact is formed in a specified thickness by rolling roll,

5-d. After that, liquid lubricant is removed.

At the sixth phase (claim item 6) of present invention, replacing the above described fifth phase, step [5-c],

Each of the following step is executed;

6-c. Next, preformed compact is formed into a specified thickness by heated rolling roll.

At the seventh phase (claim item 7) of present invention, after the aforementioned starting step, each of the following step is executed;

7-a. Amount of liquid lubricant in the preformed compact is

adjusted to be 20~47 wt%,

7-b. Preformed compact themselves are piled up using the ends, pressure adhered, and continuous long preformed compact is made, and after that,

7-c. next, preformed compact is formed into a specified thickness by rolling roll,

7-d. after that, liquid lubricant is removed.

At the eighth phase (claim item 8) of present invention, replacing the above described seventh phase, step [7-c], the following step is executed;

8-c. next, preformed compact is formed into a specified thickness by heated rolling roll.

Regarding present invention equipped with above described various phases, at least one of activated carbon and carbon black is used.

And, as fluorine containing polymer resin, polytetrafluoro ethylene (PTFE), ethylene- Tetrafluoro ethylene copolymer, chloro trifluoro ethylene -ethylene copolymer, vinylidene fluoride copolymer, tetra fluoro ethylene- perfluoroalkyl vinyl ether copolymer and the like can be used.

And as liquid lubricant, water, alcohol, propylene glycol, ethylene glycol, glycerin, white oil and the like can be used.

As to the preparation ratio of above described fine carbon powder, fluorine containing polymer resin and liquid lubricant which

constitutes kneaded product, for instance, vis-à-vis 100 wt parts of fine carbon powder, fluorine containing polymer resin 0.5~30 wt parts, and liquid lubricant 95~150 wt parts can be selected to be contained.

As to the [heated rolling roll] used at 1, 3, 4, 6 and 8th phase of present invention, the temperature is heated to be for instance, 40~350 deg C, preferably 90~120 deg c.

[Operation]

Present invention is executed, focusing on the point wherein making thin film of the preformed compact with liquid lubricant removed is done not by drawing, but by rolling roll, thereby processes are simplified and the time required to make membrane is shortened and the method is industrially highly suitable.

Because of this, the mechanism to make thin film for the preformed compact by rolling roll was studied and researched very hard, as a result, the following opinion was obtained.

As shown in figure 1, preformed compact 21 passes between a pair of rolling roll 22, and becomes sheet 23 which finished rolling.

IN figure 1, surface layer which received compression shearing force by rolling is shown by the area with hatching. It is necessary that surface layer 24, when passing rolling roll 22, is subject to fast deformation and stretches. It is speculated that if the ratio of this surface layer 24 increases vis-à-vis the entire rolled sheet 23 which finished rolling, that is if the rolled sheet thickness

is too thin, it can not follow the deformation, producing cracking and becoming small pieces. Traditionally, due to this, the minimum thickness of sheet 23 obtained by rolling was 0.6mm.

As to polytetrafluoro ethylene (PTFE), as shown in figure 2, its room temperature transfer point exists at about 20 deg C and about 30 deg C in which specific volume changes. It is speculated that this is based on the change of reverse crystal structure in the vicinity of room temperature. And, if it is heated over room temperature transfer point, the stretching of PTFE rapidly increases as in figure 3.

AS described above, in order that the deformation of surface layer 24 subject to compression shearing force follows the rolling, it is considered that PTFE is heated over room temperature transfer point, making the deformation easier.

Hence, preformed compact was rolled by rolling roll that was heated over room temperature, then, the sheet with less than 0.6mm present invention has become able to be easily and speedily produced, which had been impossible traditionally.

The speculation of the above described room temperature transfer point was done about PTFE, however, the same can be said in substance about other fluorine containing polymer resin previously listed.

And, according to the separate phases of present invention, it was found out that it is not necessary to heat rolling roll, and that if the amount of liquid lubricant in the preformed compact is

adjusted at any of the phases before rolling the roll, thin sheets can be obtained by rolling the roll. That is, if preformed compact is put into a semi-dried condition, and amount of liquid lubricant in the preformed compact is adjusted to be in the range of 10~47 wt%, there is no handling problem, plasticizing effect by residue liquid lubricant is recognized, and due to such plasticizing interaction of liquid lubricant, surface layer subject to compression shearing force deforms easily, thus making thin film is enabled, it is speculated.

However, in this case, preformed compact which contacts the rolling roller contains liquid lubricant to the extent which enable handling, and it is obtained by semi-drying the compact which contains liquid lubricant sufficiently, and even if the liquid lubricant in kneaded product is made small from the beginning, and if an attempt is made to form an equivalent product by rolling, rolling characteristics is poor, hence, sheet shape can not be produced.

In order to obtain the continuous, long preformed compact, before preformed compact themselves are piled up, and adhered by rolling, in case semi-drying of the aforementioned preformed compact are done, it is preferred that liquid lubricant in the preformed compact is adjusted to be 20~47 wt%,

[Effects of the invention]

According to present invention, e.g., thickness of 0.20~0.25 mm sheets for polarized electrode which was not possible by the

conventional rolling roll manufacturing can be produced easily and in a short time. Accordingly, using the polarized electrode thus obtained, height reduction of double layered electrical capacitor can be done advantageously.

[Embodiments]

Embodiment 1

Active carbon fibers which has polyacrylic nitrile as raw material is pulverized, and into active carbon powder which passed through 200 mesh, 120 wt parts of propylene glycol as liquid lubricant is added, they are mixed by spiral mixer. Next, into this mixture is added 5 wt parts of solid portion of PTFE water soluble dispersion (polyflrine D-1J made by Diakin Engineering Co), and kneaded, thus obtaining rubbery viscous mixture.

This viscous mixture is rolled by roll, and 1mm thick sheet shaped preformed compact is obtained.

Next, liquid lubricant in preformed compact is removed by hot wind dryer at 200 deg C.

Next, using rolling roll heated up to 90~120 deg C, preformed compact is made into thin film, producing a sheet with thickness of 0.25mm. And, as to roll temperature, the effects are seen at 40~350 deg C, however, from the stand point of ease of rolling deformation and workability, the optimum is at 90~ 120 deg C.

And, production speed of the sheet is 2m/min.

Comparison 1

Thin film making of embodiment was done by stretching, producing sheet with thickness of 0.25mm.

As to the production speed of sheets, one can find out that 0.5m/minute is the limit and compared with the embodiment 1, it is very fast.

Embodiment 2

* (summary) compared with embodiment 1, using the semidried preformed compact, thin film making at room temperature is enabled. *

Doing same as in embodiment 1, the sheet shaped preformed compact with thickness of 1mm is obtained.

Next, by 90 deg c of thermal dryer, the liquid lubricant in this preformed compact is adjusted to be 10~47 wt%.

This preformed compact is made into thin film by rolling roller at room temperature, producing sheets with thickness 0.25mm. After that, liquid lubricant in sheets is removed, thus producing sheets for polarized electrode. At this time, there was no sheet thickness change.

AS described above, the reason why thin sheets were produced without heating roll is that due to the plasticizing interaction of residue liquid lubricant, the surface layer with compression shearing force added was deformed easily.

Embodiment 3

- (summary) compared with the embodiment 2, due to the thin film making by heated roll, sheet strength improvement and one layer

thin film making was enabled *

Doing same as in embodiment 2, sheet shaped preformed compact was made which contains 10~47 wt% of liquid lubricant.

This preformed compact is made into the thin film by rolling by heated roll at 90~129 deg c, producing sheet with thickness of 0.20mm. After that, liquid lubricant in sheets is completely removed, thus obtaining sheets for polarized electrode. At this time, there was no sheet thickness change.

Regarding embodiment 1 and embodiment 2, fine cracks that had existed before making thin film still remained after rolling, sometimes, cracking developed from these parts. However, regarding embodiment 3, cracks disappeared after rolling, no cracking developed. And, the lower limit of thin film making in embodiment 1 and 2 was 0.25 mm thickness, but in embodiment 3, sheets with thickness of 0.20mm were easily obtained.

regarding above, according to embodiment 1~3, compared with the stretching method of sheet shaped preformed compact of comparison 1, due to the roll rolling, easy and fast thin sheets have become to be able to be made.

Embodiment 4

* (summary) making longer the sheet in embodiment 1

regarding embodiment 1~3, in order to make thin film for each

preformed compact, the length of obtained sheets were about 4 meter at most, continuous long product was not obtained. Embodiment 4 enables the continuous long product.

That is, doing same as in embodiment 1, 1mm thick sheet shaped preformed compact was obtained.

A plural number of preformed compact themselves thus obtained were piled up using the ends, were adhered by rolling roll, thus obtaining continuous, long preformed compact. That they were adhered was that due to the plasticizing interaction of liquid lubricant, adhesion layer easily deformed.

Liquid lubricant in long preformed compact was removed by 200 deg C thermal wind dryer.

Next, using rolling roll heated up to 90~120 deg C, long preformed compact was made into thin film by rolling, thereby continuous sheet with 0.25mm thickness was produced.

Embodiment 5

- (Summary) making long the sheets in embodiment 2*

Doing same as in embodiment 4, continuous long sheet shaped preformed compact was obtained.

Next, using 90 deg C thermal wind dryer, liquid lubricant in this long preformed compact was adjusted to be 10~47 wt%.

Next, this preformed compact was made into thin film by room temperature rolling roll, thus producing continuous sheet with 0.25mm thickness.

After that, the liquid lubricant in the sheets was completely removed, obtaining sheets for polarized electrode. At this time, there was no change in thickness of sheets.

Embodiment 6

- (summary) making long the sheets in embodiment 3*

Doing same as in embodiment 5, continuous long sheet shaped preformed compact which contains 10~47 wt% of liquid lubricant is obtained.

Next, this preformed compact is made into thin film by rolling by heated roll at 90~120 deg C, 0.20mm thick sheets were produced.

After that, liquid lubricant in sheets is completely removed, thus making sheets for polarized electrode. At this time, there was no thickness change of sheets.

Regarding embodiment 4 and embodiment 5, cracks that had existed before making thin film remained after rolling, sometimes, cracks developed from these parts. However, in embodiment 6, after rolling, cracks disappeared, no cracks developed.

Embodiment 7

- (summary) semi-dried preformed compact was made long, and made into thin film at room temperature*

Sheet shaped preformed compact which contains 20~47 wt% liquid lubricant was obtained

Next, these plural number of preformed compact themselves were piled using the ends, and adhered by rolling roll, thus obtaining

continuous long preformed compact. Here, if liquid lubricant were 20~47 wt%, due to the plasticizing interaction of this liquid lubricant, adhesion was possible.

Next, above described long preformed compact was made into thin film by rolling roll at room temperature, thus continuous sheets with 0.25mm was produced.

After that, liquid lubricant in sheets was completely removed, thus obtaining polarized electrode sheets. At this time, the thickness of sheets did not change.

Embodiment 8

- (Summary) semi-dried preformed compact was made longer, and using heated roll, made into thin film.

Doing same as in embodiment7, continuous long sheet shaped preformed compact was obtained which contained 20~47 wt% of liquid lubricant.

This preformed compact was made into thin film by rolling roll heated up to 90~120 deg C, thus producing sheets with 0.20mm thickness.

After that, liquid lubricant in sheets was completely removed, made into polarized electrode sheets. There was no change of sheet thickness.

Regarding embodiment 7, a few fine cracks that had existed before making thin films remained, sometime cracks developed from these parts. After rolling, cracks disappeared, no cracks developed.

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Summarizing the above described embodiment 1~8 and comparison example 1, the following table 1 shows it.

Table 1

	Method to make thin film	Thickness of sheet (mm)	Sheet forming speed
Embodiment 1	Rolling roll	0.25	2 meter/min
Embodiment 2		"	
Embodiment 3		0.20	
Embodiment 4		0.25	
Embodiment 5		"	
Embodiment 6		0.20	
Embodiment 7		0.25	
Embodiment 8		0.20	
Comparison 1	Stretching	0.25	0.5m/min

According to table 1, one can tell that polarized electrode sheet with thickness of 0.20~0.25mm which was not possible by the traditional rolling roller can be produced easily and in short time.

And, using the sheets respectively obtained from embodiment 1~8 and comparison case 1, ones which were punched out into disk shape were used as polarized electrode 4a and 4b shown in figure 4, capacitor cell 2 was made, these capacitor cell 2 were assembled, and double layered electrical capacitor 1 as shown in figure 5 were produced. The product height H of double layered electrical capacitor 1 thus obtained, and static electricity capacity were measured, its

measurement result was shown in the following table 2. In table 2, static electricity capacity was calculated as follows: it was charged at 2mA fixed current, and the time was measured in which inter-terminal voltage climbed from 2V to 4V, the value was used for calculation.

Table 2

	Product height H	Static electricity capacity
Embodiment 1	5.5mm	60 mF
Embodiment 2	"	59 mF
Embodiment 3	5.0mm	51 mF
Embodiment 4	5.5 mm	59 mF
Embodiment 5	"	60 mF
Embodiment 6	5.0mm	50 mF
Embodiment 7	5.5 mm	59 mF
Embodiment 8	5.0 mm	51 mF
Comparison 1	5.5 mm	58 mF

4. Simple explanation of drawings

Figure 1 is a drawing showing the rolling roll process applied for preformed compact. Figure 2 is a graph showing the relationship between specific volume of polytetra fluoro ethylene and temperature. Figure 3 is a graph showing the relationship between the stretch in the stretching of polytetrafluoro ethylene and temperature. Figure 4 is a cross section drawing showing the capacitor cells contained in double layered electrical capacitor.

Figure 5 is a cross section drawing showing the double layered

electrical capacitor made by using capacitor cells shown in figure 4.

Regarding drawings, 1 is a double layered electrical capacitor; 4a, 4b are polarized electrode; 21 is preformed compact; 22 is rolling roll; 23 is a sheet for rolling

図 1

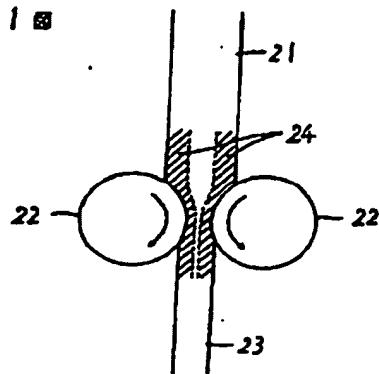


図 2

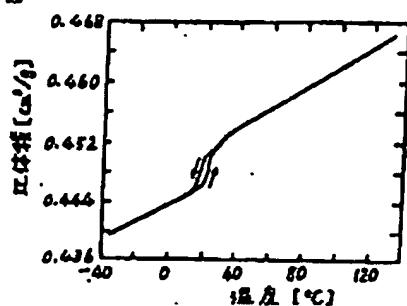


図 3

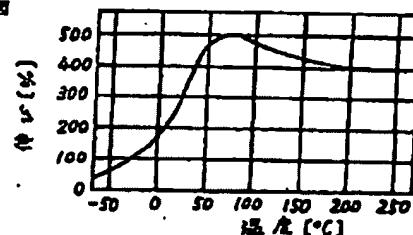


図 4

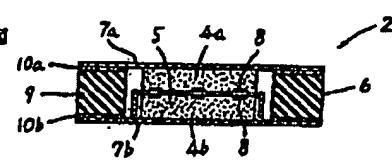


図 5

